ON POSSIBLE ELECTRONIC TRANSITIONS IN Pr^{+++} IONS AND THE ABSORPTION SPECTRA OF THE SAME IN SOLUTION AND IN CRYSTALS.*

By P. C. MUKHERJI,

Research Fellow, Calcutta University.

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Plate XV.

ABSTRACT. The absorption spectra of Pr^{+++} ions in solution and in crystals have been investigated here over the region from 900 mμ to 200 mμ. In solution the intensity of absorption has been measured over the visible region with a double monochromator. Using large single crystals of $PrCl_3$, $7H_2O$, the changes brought about at liquid air temperature in the nature of the different groups of absorption lines and bands have been studied. A preliminary classification of these groups of absorption lines and bands is given based on the assumption that they are due to inner forbidden transitions. Every transition is supposed to give rise to a group. In this process of classification the term values of Pr IV have been calculated from those of La II and compared with the mean frequencies of the different groups obtained in absorption. The Van Vleck's theory of the absorption spectra of rare earths in solids has been discussed. A scheme of classification of the rare earth spectra presented by Ellis has been noted and the divergences explained.

INTRODUCTION.

In a previous paper [1] the absorption spectra of Nd^{+++} ions in solution and in crystals were investigated by the writer over a wide range of temperature. A classification of the groups of sharp absorption lines and bands, obtained with large single crystals at low temperature, was also attempted there. It was shown that the groups of sharp lines and bands originate from the forbidden transitions inside $4f$-shell. The finer structure inside each group, due to the decomposition of the energy levels in the crystalline field as well as to the superposition of the lattice vibrations, was not taken into consideration. The object of the present paper is to report the results of a similar investigation carried on with Pr^{+++} ions in solution and in crystals. It is intended also to classify their spectra broadly.

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EXPERIMENTAL INVESTIGATIONS.

(*a*) The investigations were precisely similar to those described in the case of Nd^{+++} ions. The absorption spectra of the ions in solution were investigated from 900 mμ to 200 mμ. But in the present case the sharp lines and bands were found to be limited to the visible region. This is due to the fact that Pr^{+++} ions do not possess any sharp absorption spectra in the ultra-violet; in the infra-red they lie beyond 900 mμ up to which it was possible to photograph with the plates available here. In all there were five bands, a double band on the red side and three bands in the blue and violet.

The quantitative study of the absorption of Pr^{+++} ions in solution was carried out with a Hilsch double monochromator, a K-photo cell and a Wulf's string electrometer. The investigation was limited to the visible region only. The results of the measurement are given in table I. A curve showing the variation of the percentage of absorption with wave-length is given in figure 1.

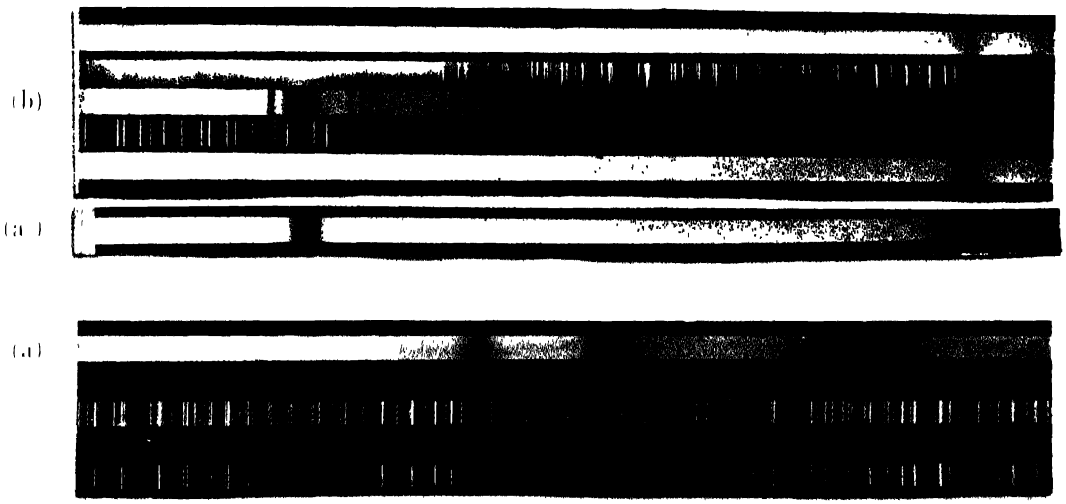
TABLE I.

(Positions of the absorption maxima obtained with the double monochromator.)

	Concentration	Thickness.	Position of absorption maxima.	P. c. of Absorption.
I (*a*)	15%	1 cm.	5970 Au.	14·5
(*b*)	,,	,,	5855 ,,	22
II	,,	,,	4832 ,,	28·5
III	,,	,,	4684 ,,	38
IV	,,	,,	4436 ,,	57·2

(*b*) The investigation of the absorption spectra at low temperature was carried out with large single crystals of $PrCl_3, 7\ H_2O$. The crystals were prepared in the laboratory by slow evaporation of the saturated solution as described in the previous paper, when very fine hexagonal crystals were obtained. They were ground to different thicknesses and sealed in glass cells. A Hilger E_1 spectrograph with glass optical parts was used. The spectra were photographed at the room temperature and at that of liquid oxygen. At the low temperature the exposure varied from 15 to 25 minutes using "Kodak Superpan Cutfilms."

It was found that at the temperature of liquid oxygen the diffuse double band on the red side was resolved into a large number of extremely sharp lines



Absorption Spectra of ($PrCl_3$, 7 H_2O) crystal in the visible region.

(*a*) at room temperature
(*b*) at liquid air temperature
(*a'*) at room temperature with thicker crystal

and bands. The three bands in the blue and violet regions did not show such extremely fine structure. The first two of these three bands were decomposed into a number of rather diffuse narrower bands, while the third band in the violet remained unaffected. They perhaps require still lower temperature for getting resolved into extremely sharp and narrow components. The thickness of the crystal used was 1.5 m.m. In order to investigate still weaker components, if there be any, a crystal of thickness 3 m.m. was used. It was found that a few weaker components were added to the group of absorption lines in the red. A new group of very faint lines also appeared in the green region. These are shown in plate XV, and the wave-lengths and wave-numbers of these lines and bands are given in the table II.

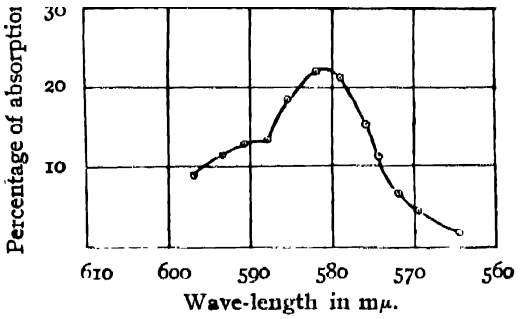


FIGURE 1(*a*).

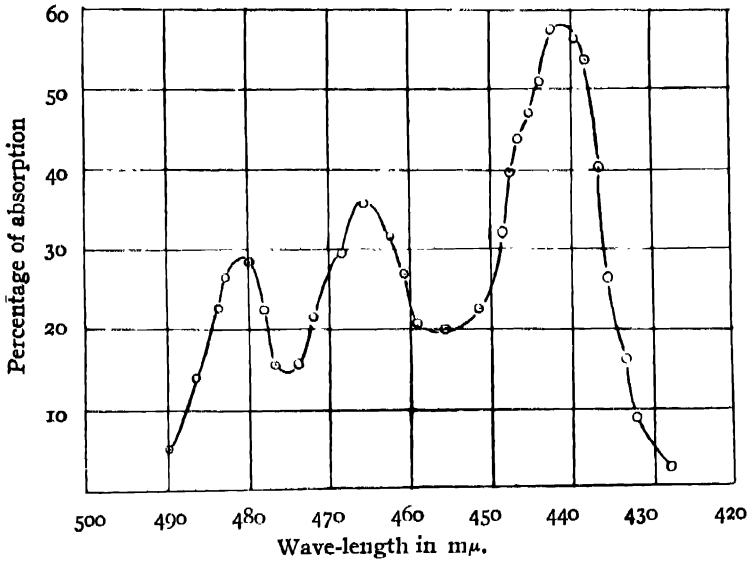


FIGURE 1(*b*).

DISCUSSION OF RESULTS.

It is apparent from the table II that Pr^{+++} ions show five groups of absorption lines and bands in the visible region. Over and above these five groups, there are three groups in the infra-red which it was not possible to photograph

TABLE II.

(The wave-lengths and wave-numbers of the lines and bands obtained with single crystals at different temperatures.)

Room Temp.		Oxygen Temp.		Remarks.
	λ (Å)	λ (Å)	ν (Cm^{-1})	
I (*a*)	5993.5—	5991.1	16,686 8	At the temperature of liquid oxygen the diffuse band is resolved into several narrow and sharp components. The intensity of absorption increases.
	5972.1	5984.1	16,706.3	
		5981	16,715.0	
		5955.2	16,787.4	
(*b*)	5935·4—	5946.1	16,813.1	
	5884.9	5938.2	16,835.5	Do.
		5927.8	16,865	
		5903.2	16,935.3	
(*c*)		5838.5	17,122.9	The three faint and rather diffuse lines split up into sharp doublets and some new lines appear.
		5830.5	17,146·4	
		5800.7	17,234 5	
	5795.7	5794.8	17,252.1	
	5768	5773·9	17,314·5	
		5759	17,359·3	
	5744.6	5753·7	17,375·3	
		5736.1	17,428.6	
II		5263.9	18,992.1	
		5234·6	19,098·4	
	5230.9	5229.4	19,117.3	Do.
	5215 4	5215·8	19,167.2	
		5200.5	19,223·6	
III		4878.9	20,490.7	The broad band is resolved into narrower bands, but they remain slightly diffuse even at the low temperature.
		4864.5	20,551.4	
	4845.9—	4847.1	20,625.2	
	4833.8	4843.7	20,639.6	
		4841.2	20,650 3	
		4834 6	20,678.5	
		4826.3	20,714	
IV		4719 2	21,184.1	
	4715.2—	4713.2	21,211.1	
	4703.4	4707·3	21,237·7	
		4696.6	21,286.1	Do.
	4692.5—	4689.5	21,318.3	
	4682.8	4670.4	21,405 4	
V	4431.0—	4434—	22,597—	
	4473·4	4478	22,325	The band remains un

here. The first two of these were first investigated in solution by P. Lueg[2] using a thermopile and a galvanometer and were found at 2μ and 1.54μ. Later Freyman and Takavorian[3] observed the third in the near infra-red with a thalofide cell. It was found to be a weak band having its crest at 10,182 Å. Gobrecht[4] made precision measurements of these bands using borax beads containing the borate of the element. He photographed the third group on specially prepared infra-red sensitive plates and obtained a number of sharp weak absorption lines using crystals of $Pr_2(SO_4)_3$, $8H_2O$. The centre of gravity of each of these groups as well as those observed here are given in table III. The relative intensities of the groups are also noted there.

TABLE III.

(The positions of the centres of gravity of all the different groups observed in Pr^{+++} ions.)

	Intensity.	C. G. of different groups	Nature.
I	Strong	5,200 cm^{-1}	A broad band.
II	Very strong	6,950 ,,	Possesses some structure.
III	Weak	9,835 ,,	Consists of sharp components at low temperature.
IV (*i*)	Strong	16,811 ,,	Do.
(*ii*)	Fair	17,275 ,,	Do.
V	Very weak	19,107 ,,	Do.
VI	Strong	20,602 ,,	Components are diffuse at low temperature.
VII	Strong	21,294 ,,	Do.
VIII	Very strong	22,461 ,,	One broad band.

A preliminary classification of these eight groups of absorption lines and bands will be attempted here on the supposition that they are due to the transitions of the $4f$-electrons inside the $5s$, p-shell. Van Vleck [5] discussed the origin of the spectra of the rare earth ions in solids and showed that their extremely sharp nature and the very feeble intensity could be explained on the assumption that they are due to the inner forbidden transitions. The different possibilities of such transitions as enumerated by him will be referred to later. In Pr^{+++} ions containing two $4f$-electrons the different inner states allowed by Russell-Saunders coupling are given by $^3(P, F, H)$ and $^1(S, D, G, I)$. The ground state according to Hund's rule is given by $^3H_4$; it also explains the magnetic properties of the ion. It now follows from above that electronic transitions between the ground state and the other allowed states give rise to the different groups of absorption bands. Further the appearance of all the bands in monochromatic excitation indicates that all transitions take place from the ground state. The multiplicity of lines inside each group, shown by crystals at low temperature, is taken to be an effect of the crystalline field and also of the coupling of the electronic levels with the lattice vibrations. They will not be discussed here. The C.G's of the groups will instead be regarded as representing the frequencies of the corresponding electronic transitions in absence of any field, and to these the different transitions will be assigned. This will require a knowledge of the relative positions of the different excited levels. According to Hund's rules it follows that among the triplet levels the relative arrangement will be given by $^3P > ^3F > ^3H$ and similarly among the singlets. But it is not possible to obtain any relation between the triplet terms on the one hand and the singlet ones having much

higher values of orbital moment on the other.* It is proposed therefore to obtain this information from the evidences of emission spectra.

The emission spectra of Pr IV have not yet been investigated. It is found however that in the analysis of the emission spectra of La II by Meggars and Russell [6] there are several terms to which the electronic configuration $4f^2$ is assigned. These terms are quite analogous to those of Pr^{+++} ions whose transitions are considered here and it seems reasonable to take the relative arrangement of the terms from these data. The values of the corresponding terms of La II together with their symbols are presented in table IV. For convenience, in

TABLE IV.

(Term values of different states of La II with a configuration $4\ f^2$.)

Symbol.	J	Term value (cm^{-1})	$\Delta\nu$	Relative position of terms
^3H	4	55,107·25		0
			874·84	
	5	55,982·09		874·84 cm^{-1}
			855·85	
	6	56,837·94		1,730·69 ,,
^3F	2	57,399·58		2,292·33 ,,
			518·92	
	3	57,918·50		2,811·25 ,,
			340·91	
	4	58,259·41		3,152·16 ,,
^1G	4	59,527·60		4,420·35 ,,
^1D	2	59,900·08		4,792·83 ,,
^1I	6	62,408·40		7,301·15 ,,
^3P	0	63,463·95		8,356·70 ,,
			139·23	
	1	63,603·18		8,495·93 ,,
			675·74	
	2	64,278·92		9,171·67 ,,
^1S	0	69,505·06		14,397.81 ,,

addition to the absolute term values, their values relative to $^3H_4$ are also given in the table.

Apart from a knowledge of the relative position of the energy levels of Pr^{+++} which is obtainable from these data, it is also possible to calculate their term values. The difference between their values is due to (*a*) the higher ionisation of the Pr^{+++} ions and (*b*) the slightly greater value of the effective nuclear charge

* In the classification of the Nd^{+++} spectra this difficulty did not arise, as the allowed doublet terms with much higher values of L could not be fitted into the scheme of classification on account of their large separations and therefore were not taken into consideration.

of the latter. The effect of these will be to increase the intervals between the energy levels by a constant factor. From a comparison of the separation between the components of the ^3H multiplet, obtained for La II and that calculated in the case of Pr^{+++}, it is found that the factor $\frac{2115}{875}$ is approximately 2·41. The values of the different terms of Pr^{+++} ions calculated from those of La II by multiplying with this factor are given in Table V.* The C.G's of the groups observed in absorption are placed side by side with the calculated terms, with which they more or less agree. The changes in L and J occurring in these transitions are given in the last column.

TABLE V.

(Calculated term values of Pr IV and centres of absorption groups of Pr^{+++} ions.)

Symbol	J	Calculated 'ν'	Observed. 'ν'	ΔL ; ΔJ
^3H	4	0		
	5	2,100 cm^{-1}	...	
	6	4,154·4 ,,	...	
^3F	2	5,500·8 ,,	5,200 cm^{-1}	−2 ; −2
	3	6,746·4 ,,	6,950 ,,	−2 ; −1
	4	7,564·8 ,,		
^1G	4	10,608 ,,	9,835 ,,	−1 ; 0
^1D	2	11,740·8 ,,	—	
^1I	6	17,522·4 ,,	17,043 ,,	1 ; 2
^3P	0	20,066·8 ,,	20,602 ,,	−4 ; −4
	1	20,390·4 ,,	21,294 ,,	−4 ; −3
	2	22,012·8 ,,	22,461 ,,	−4 ; −2
^1S	0	34,555·2 ,,	—	

* As the different 4*f*-electronic levels are due to different combinations of the 'l' and 's' vectors of these electrons, it follows from general reasoning that here the inter-multiplet and the intra multiplet intervals will be the same function of the effective nuclear charge. It is because of this that the multiplication of all the intervals by the same constant factor is possible in this case.

It will be noticed in table V that the agreement between the calculated terms of Pr IV and the mean absorption frequencies of Pr^{+++} ions is fairly good. Besides this there are also other reasons in favour of the transitions assigned for the particular groups. Van Vleck showed that in the process of absorption by rare earth solids the strongest radiation will be quadrupole in nature allowing ΔL or $\Delta J = \pm 2, \pm 1$ and 0. Further on account of the asymmetry, either present in the crystalline fields or brought about when the electron is set in vibration, transitions are possible where ΔL or ΔJ reaches a value up to ± 4. From the last column of the table it is apparent that these allowed changes are not exceeded in any case. Also the relative intensity of the absorption groups is found to be greater the lower the change occurring in the value of J, excepting the case $\Delta J = 0$, where weak radiation is expected. One point which is very significant is that in the above table no absorption group is specified for the transition $^3H_4 \longrightarrow {}^3F_4$. This may be due to the fact that on account of the low dispersion in the infra-red the corresponding relatively weak group was overlapped by the very strong group preceding it. This also accounts for the rather large interval between I and II which is found to be 1740 cm^{-1} while the calculated one is 1270 cm^{-1}. Gobrecht represented this transition by the weak group at 9835 cm^{-1}. But its interval from group II, which is 2,885 cm^{-1}, seems to be rather too high as compared with the calculated splitting, *viz.*, 1,690 cm^{-1}.

In this preliminary classification it is not intended to deal with the origin of the fine structure shown in many of the groups. They could not be investigated in detail in some of the groups at the low temperature available in this laboratory. These have, however, been extensively investigated by Spedding and his co-workers [7] during the progress of the present work. From a study of the absorption spectra of many of the rare earth ions, Ellis [8] has proposed a scheme in which the successive excited inner states appear above their normal ground states. In Pr^{+++} they are respectively $^1I_6$, $^3P_{0,1,2}$. In the classification given above the successive excited states are represented by $^3F_{2,3,4}$; $^1G_4$; $^1I_6$; $^3P_0$, $I_{0,1,2}$. Although he has not yet published the complete account, it appears from a comparison of the two that he has perhaps taken into consideration only the absorption spectra in the visible region.

In conclusion, the writer desires to express his grateful thanks to Prof. D. M. Bose for his kind interest and advice during the progress of the work.

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PALIT PHYSICAL LABORATORY,
92, UPPER CIRCULAR ROAD.
CALCUTTA.